

Inhibition of Calcium Carbonate Scale Formation in Water-Mono Ethylene Glycol Solutions by Water Soluble Polymers

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ABSTRACT

Calcium carbonate polymorphs are encountered in water intensive industrial processes and gas and petroleum production operations. The presence of water-soluble polymers at very low concentrations (ppm) is known to affect nucleation and/or crystal growth of calcium carbonate polymorphs. The presence of Mono Ethylene glycol (MEG) in supersaturated solutions has been found to affect both kinetics and the morphology of calcium carbonate. In the present study, the effect of acrylate polymers and copolymers with sulfonic and styrene units on the formation of calcium carbonate, in supersaturated solutions, prepared in mixtures of water-MEG (0-60% v/v MEG). The inhibitors tested included poly acrylic acid (PAA), and a Ter polymer (Polymer acrylic acid sulfonic acid sulfonated styrene at concentrations of 1 to 5 ppb). The kinetics of calcium carbonate were measured at constant supersaturation. Rate reduction in the presence of the test inhibitors was comparable or more effective in comparison with the case in aqueous solutions. The initial formation and stabilization of the metastable phases of aragonite and vaterite was identified with X-ray diffraction (XRD) and scanning electron microscopy (SEM). Test inhibitors seemed to retard transformation of the least stable vaterite.

Key words: scale, calcium carbonate, inhibition, mono-ethylene glycol, acrylic polymers

INTRODUCTION

The formation of tenaciously adhering calcium carbonate (CaCO_3) scale deposits is a commonly encountered problem in water intensive industrial processes.¹ These deposits once developed is very hard to remove resulting in extensive shutdown periods for necessary replacements of the clogged parts of the installations. Calcium carbonate is encountered in three polymorphic anhydrous forms, and two hydrate salts (mono and hexahydrate). The anhydrous polymorphs include vaterite, aragonite and calcite in the order of increasing thermodynamic stability (lower solubility) have been identified in scale deposits on heat exchangers, water treatment equipment and in secondary oil production processes in which water is used for the displacement of the oil phase. Most often, scale prevention processes involve use of water soluble polymers, which at very low concentrations (in the order of a few ppm) are capable of controlling nucleation and/or crystal growth of calcium carbonate polymorphic phases.^{2,3} The anti-scaling efficiency of these compounds towards the formation of specific sparingly soluble salts, depends to a large extent on the type of their functional groups. The presence of water soluble polymers in the aqueous medium in which nucleation and crystal growth takes place in several cases has a profound effect on the morphology of the forming crystals because of their preferential adsorption on certain crystal faces, the growth of which is inhibited. Moreover, the kinetic stabilization of transient phases (mainly vaterite) has been reported to depend on molecular characteristics including molecular weight, shape

etc.^{4,5} Typical commercially available inhibitors used in a large number of industrial sectors and processes are polyacrylic and polyphosphonic polymers.^{5,6} In oil and gas industry mono-ethylene glycol (MEG) is used as inhibitor of hydrates.⁷ The presence of MEG mixed with water is expected to affect solute-solvent interactions of the inhibitor molecules and hence it may affect the efficiency of inhibitors. There are several reports in the literature concerning the effect of polyacrylic compounds on the formation of calcium carbonate but for the most part they are limited in aqueous systems.^{8,9} In the present work the formation of calcium carbonate from supersaturated solutions in the presence of MEG (concentrations 0-60% v/v) was investigated in the presence of polyacrylic acid of two different molecular weight values: PAA1 (MW 2,000) and PAA2 (MW 6000). Moreover, the presence of the water-soluble acrylic copolymer PAS was investigated. Precise and reproducible measurements of the kinetics of precipitation of calcium carbonate were done at conditions of constant supersaturation. All polymeric compounds tested are commercialized as scale and corrosion inhibitors and they are often used in combination with bacteriocides for the suppression of microbially induced corrosion. The stability domain of the calcium carbonate system was investigated and the morphology and mineralogical composition of the precipitates forming in the presence of MEG and of the inhibitors. The presence of MEG in the aqueous media reduced the solubility of calcium carbonate⁶ and is therefore expected to favor the formation of this salt.

EXPERIMENTAL PROCEDURE

All experiments were done in a double walled glass reactor, volume totaling 220 mL and was thermostatted with water circulated through the walls with the help of a circulating thermostat at $25^{\circ}\pm 0.2^{\circ}\text{C}$. the supersaturated solutions were prepared inside the reactor mixing equal volumes of calcium chloride (CaCl_2) and sodium bicarbonate (NaHCO_3) solutions, prepared from stock solutions of the respective crystalline reagents. The solutions mixing was done under constant stirring. In the presence of MEG, the CaCl_2 and NaHCO_3 solutions were prepared as mixtures of MEG with the aqueous solution on the basis of the partial molar volumes of the aqueous phase and the respective of MEG. pH value of the solutions was adjusted by the addition of standard NaOH solution (0.1M) as needed. The ionic strength of the supersaturated solutions was constant and adjusted with the appropriate amount of sodium chloride stock solution. The solutions pH was measured by a glass-saturated silver chloride electrode, suitable for measurements of aqueous and water miscible non-aqueous solutions. The standardization of the electrode probe was done using NIST standard buffer solutions considering the presence of MEG. pH was monitored through the appropriate interface and software by a computer. pH drop as small as 0.005 pH units, corresponding to the initiation of calcium carbonate precipitation, triggered the addition of titrant solutions from two mechanically coupled precision syringes. The solutions in the two syringes consisted of CaCl_2 and NaHCO_3 at carefully calculated concentrations so that the activities of all ions in the supersaturated solutions were kept constant. A schematic diagram of the experimental setup is shown in Figure 1. The concentrations of the titrant solutions in the syringes were calculated according to the stoichiometry of Ca^{2+} and carbonate ions in the precipitate, i.e. $\text{Ca}^{2+}:\text{CO}_3^{2-}=1:1$

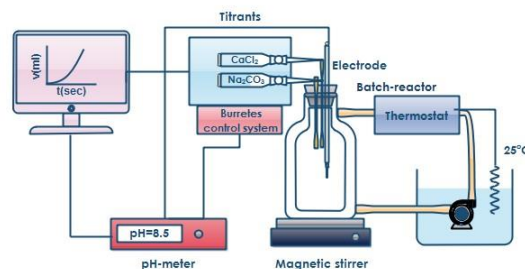


Figure 1: Schematic diagram of the experimental setup for the investigation of calcium carbonate formation at constant supersaturation in the presence of MEC and polyacrylic inhibitors

During the precipitation process, in all experiments, the constancy of the solutions supersaturation was verified by random sampling, filtration of the suspensions through membrane filters (0.20 μm) and analysis of the filtrates for calcium with atomic absorption spectrometry. The solid precipitate past each precipitation run was collected by filtration through membrane filters and was characterized by powder X-Ray diffraction (XRD) and for the morphology with scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

The driving force for the precipitation of calcium carbonate from the respective supersaturated solutions was proportional to the supersaturation ratio, SR:

$$SR = \log \frac{(Ca^{2+})(CO_3^{2-})}{K_{s,\chi}^0} \quad (1)$$

Where parentheses denote the activities of the respective ions and $K_{s,\chi}^0$ is the thermodynamic solubility product of the respective solid χ . The thermodynamic equilibrium calculation software PHREEQC¹⁰ which takes into consideration all equilibria involved,¹¹ was used for the calculation of the free ion activities in the supersaturated solutions. As already mentioned, during precipitation both the solution pH and the added volume of the titrant solutions were recorded as a function of time. From the respective plots the rates of precipitation at conditions of constant supersaturation, R_p ($\text{mol CaCO}_3 \cdot \text{min}^{-1} \cdot \text{s}^{-1}$), were calculated from equation (2):

$$R_p = \frac{dV}{dt} \frac{C}{m \times SSA} \quad (2)$$

Where dV/dt is the slope of the titrant solutions added as a function of time (linear plot), C a coefficient dependent on the rate of precipitation determining the rate of addition of titrant solutions to maintain supersaturation, m is the mass of crystals serving as a substrate for the growth of nucleated calcium carbonate and SSA the respective BET specific surface area of the crystals. In the case of spontaneous precipitation, the corresponding rates, R_{sp} , were measured at the very beginning of the V-t plots so that the solid formed by precipitation did not affect the overall rate of precipitation. In this case the rates ($\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$) were calculated according to equation (3):

$$R_{sp} = \frac{dV}{dt} C \quad (3)$$

It should be noted, that spontaneous precipitation, taking place at relatively high supersaturation is needed for the definition of the stability domain of the system of the